

Growth of Controlled Diameter Single-Walled Carbon Nanotubes

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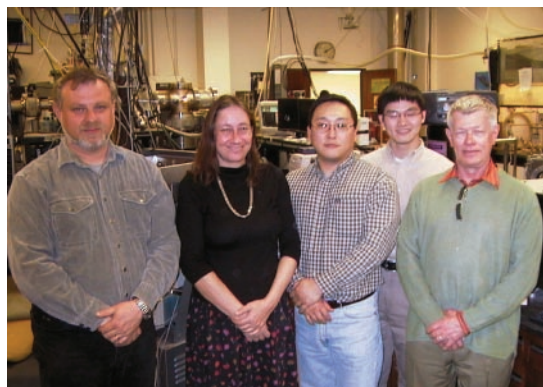
The electronic properties of single-walled carbon nanotubes (SWNTs) depend on their diameter and the chiral angle along which a single graphene sheet is rolled in a cylinder. The selective growth of SWNTs of predetermined diameters allows the synthesis of SWNTs with uniform electronic properties, which are required for electronic applications. We have shown that SWNTs can be produced with a narrow distribution of diameters centered at different discrete values. The average size of the cobalt (Co) clusters used as catalysts for SWNT growth has been determined by extended x-ray absorption fine structure (EXAFS) spectroscopy at beamline X23A2.

Catalytic processes that provide more than 90% selectivity to single-walled carbon nanotubes (SWNTs) have been developed, but catalysts that allow the engineered control of the mean diameter of SWNTs are not available. Since the properties of SWNTs depend on the tube diameter, a catalyst that selectively produces a given, preselected size is technologically important. Here we demonstrate that the cobalt-based catalyst Co-MCM-41 (where MCM stands for "mobil crystalline material") can be used to control the cluster size of cobalt metal in the pores. This, in turn, catalytically produces SWNTs with a narrow distribution of diameters (± 0.05 nm) in the 0.5 to 0.8 nm range.

We chose Co as the catalytic material because it has been demonstrated to be a selective catalyst for SWNTs, especially when stabilized against total reduction. We hypothesized that if Co were isomorphously substituted for silicon (Si) in MCM-41, the MCM-41 matrix would stabilize the Co against total reduction and sintering. Since catalyst metal particle size has been hypothesized to control tube diameter, we studied whether catalyst pore size could be used to control Co cluster size and, thus, SWNT diameter. Four catalysts with pore diameters of about 1.9, 2.2, 2.6, and 2.9 nm (as determined by the classical Barrett-Joyner-Halenda method) were prepared hydrothermally using C10, C12, C14, and C16 organic templates, where 10, 12, 14, and 16 denote the number of carbon atoms in the alkyl chain of the template. The diameters of the SWNTs (synthesized by the disproportionation of carbon monoxide, i.e. the Boudouard reaction) were estimated from the nitrogen adsorption isotherms and high-resolution transmission electron microscope (TEM) imaging, with the former occurring after hydrofluoric acid purification and the latter occurring before the removal of the SWNTs from the catalysts. These estimates were consistent with data from UV-visual/near-infrared absorption

spectroscopy, multiple excitation wavelength Raman, and fluorescence (the last two techniques were only used for the C16 template).

In **Figure 1** the average SWNT diameter, determined from ni-



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trogen isotherms, is plotted against the Co-MCM-41 pore size (also determined from nitrogen desorption isotherms) and compared with the inner diameter of the SWNT, which was estimated from TEM. A remarkable linear correlation between the synthesized SWNT and the Co-MCM-41 pore size is observed. It is apparent, however, that the SWNT diameter control is not a result of simple geometric or mechanical constraint by the pore walls.

We hypothesize that the actual sites for SWNT growth are Co metal clusters, which is consistent with previously proposed growth mechanisms, and that the diameters of the SWNTs are controlled by the Co metal cluster size. The metal cluster size, in turn, is determined by the stability of the Co^{2+} ions in the MCM-41 silica wall. Controlling the cluster size is done using the metal precursor as a cation constituent of the MCM-41 pore wall, which stabilizes the metal against reduction and migration/sintering during catalyst preparation. The smaller the pore diameter of the Co-MCM-41, the more resistant is the Co^{2+} against reduction, and the smaller is the Co metal cluster that is formed. We have confirmed this hypothesis using the temperature-programmed reduction method. We used EXAFS to measure the Co cluster size in variable-diameter Co-MCM-41 samples exposed to the Boudouard reaction under identical conditions. The EXAFS results indicate increased Co cluster sizes in MCM-41 with larger pore diameters, as shown in **Figure 2**.

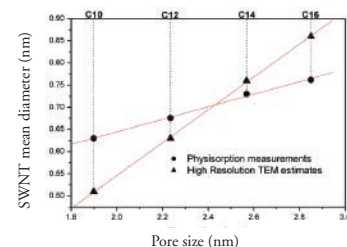


Figure 1. SWNT diameters determined by nitrogen physisorption and HR-TEM for samples produced using catalysts with different pore sizes.

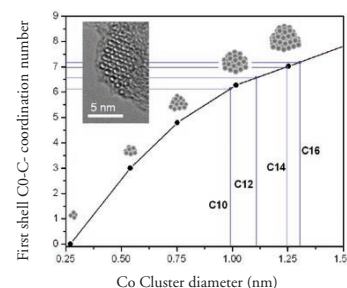


Figure 2. Size of metallic Co clusters determined from Co-Co coordination number estimated determined by fitting the EXAFS spectra recorded for Co-MCM-41 samples reacted with CO under identical conditions. The cluster sizes were calculated assuming a (111) truncated hemispherical cuboctahedron model for the cobalt clusters. The TEM image inset shows a SWNT bundle in a closed hexagonal packing characteristic only for uniform diameter nanotubes.